

University of Groningen

A new mechanism for radiation damage processes in alkali halides

Dubinko, V. I.; Turkin, A. A.; Vainshtein, D. I.; den Hartog, H. W.

Published in:
Journal of Applied Physics

DOI:
[10.1063/1.371639](https://doi.org/10.1063/1.371639)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1999

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Dubinko, V. I., Turkin, A. A., Vainshtein, D. I., & den Hartog, H. W. (1999). A new mechanism for radiation damage processes in alkali halides. *Journal of Applied Physics*, 86(11), 5957 - 5960.
<https://doi.org/10.1063/1.371639>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

A new mechanism for radiation damage processes in alkali halides

V. I. Dubinko^{a)} and A. A. Turkin

National Science Center Kharkov Institute of Physics and Technology, 310108 Kharkov, Ukraine

D. I. Vainshtein and H. W. den Hartog

Solid State Physics Laboratory, University of Groningen, Nijenborgh 4, NL-9747 AG Groningen, The Netherlands

(Received 11 March 1999; accepted for publication 24 August 1999)

We present a theory of radiation damage formation in alkali halides based on a new mechanism of dislocation climb, which involves the production of V_F centers (self-trapped hole neighboring a cation vacancy) as a result of the absorption of H centers of dislocation lines. We consider the evolution of all experimentally observed extended defects: metal colloids, gas bubbles, and vacancy voids. Voids are shown to arise and grow large due to the reaction between F and V_F centers at the surface of halogen bubbles. Voids can ignite a back reaction between the radiolytic products resulting in decomposition of the irradiated material. © 1999 American Institute of Physics. [S0021-8979(99)00623-4]

I. INTRODUCTION

In the alkali halides, the principal radiation damage consists of *bubbles of fluid halogen* formed by agglomeration of H centers and of the complementary inclusions of alkali metal (*colloids*) formed by agglomeration of F centers.¹ Both H and F centers are primary radiation defects in the halide sublattice. The H center is a halide interstitial ion with a trapped hole, and an F center is the vacancy in the halide sublattice with a trapped electron. There is evidence² for the formation of numerous *perfect* interstitial dislocation loops, which evidently require both interstitial halogen and interstitial alkali metal. From our results³⁻⁵ obtained for NaCl, which had been irradiated with 0.5 MeV electrons up to fluences 6×10^{18} electrons/cm² (about 300 Grad or 30 displacements per anion), it follows that large *vacancy voids* (up to hundreds of nm in size) are formed (Fig. 1). The void formation requires agglomeration of both cation and anion vacancies, which cannot be explained by the conventional Jain and Lidiard model.⁶ According to the latter, the *dislocation bias* for H centers if the driving force for the colloid growth in alkali halides exactly in the same way as for the *void growth in metals* under irradiation. However, the mechanism of dislocation climb² used in the Jain and Lidiard model, requires two H centers and leaves behind a molecular center, i.e., halogen molecule in a stoichiometric vacancy pair (a stoichiometric vacancy pair consists of two adjacent vacancies, one in the cation and one in the anion sublattice). Thus, only dispersed molecular centers and metal colloids can be formed according to the Jain and Lidiard model. Below we present a new model of radiation damage formation in alkali halides, which would allow for the creation of halogen bubbles and voids instead of dispersed molecular centers.

II. MECHANISM OF DISLOCATION CLIMB

When an H center approaches a dislocation, it is assumed to displace a lattice cation and form with this ion a

stoichiometric interstitial pair (needed for the dislocation climb) *leaving behind a hole trapped next to a cation vacancy* (see Fig. 2). The latter is known as the V_F center, which is a mobile “antimorph” of the F center (electron trapped in an anion vacancy). This reaction is more straightforward than the one proposed by Hobbs *et al.*,² and which is used in the Jain and Lidiard model. The new reaction requires only one H center as compared to two H centers meeting at the dislocation core, according to the existing mechanism.² This is a rather improbable event during irradiation at elevated temperatures, where F centers are mobile as well, and their fluxes to dislocations differ from H center fluxes only due to the dislocation bias.

In our case, the dispersed halogen molecules can be produced as well. Indeed, mobile V_F centers can subsequently recombine with each other to form a halogen molecule sitting in a double vacancy pair (i.e., in two adjacent stoichiometric vacancy pairs). This can be a nucleus of a halogen bubble that is formed by a subsequent absorption of H centers as described in the next section.

However, what is more important is that the V_F center is the antimorph of the F center so that their mutual recombination would result in production of a stoichiometric vacancy pair. Such a recombination is expected to take place first at halogen bubble surfaces since coherent colloids are assumed to be transparent for V_F centers and do not trap them. Indeed, the V_F center is a defect in the cation sublattice that is not damaged by coherent colloids. An important consideration is that the production of V_F centers by dislocations requires excess of incoming H centers over F centers, since the latter induce a back reaction (Fig. 2). Similarly, the production of vacancy pairs at the bubble surface requires an excess of incoming F centers over H centers. This means that all reactions involved in the production and absorption of V_F centers at extended defects are controlled by the biases for absorption of H centers or F centers. We will consider the biases in more detail.

^{a)}Electronic mail: h.w.den.hartog@phys.rug.nl

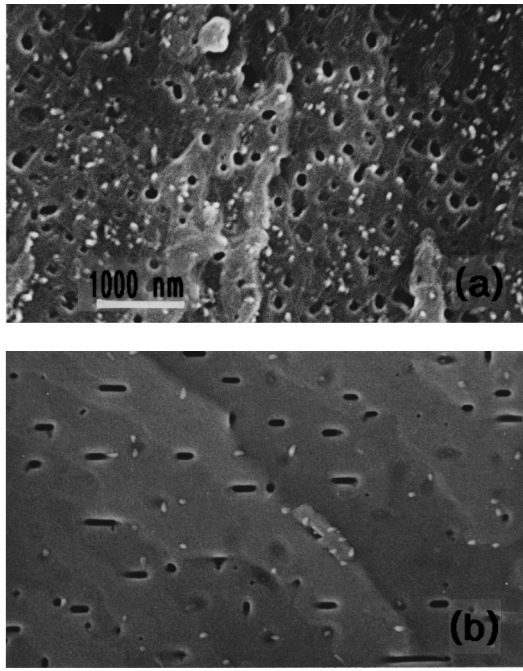


FIG. 1. SEM micrographs showing vacancy voids in doped and natural NaCl samples irradiated with 0.5 MeV electrons to a dose of 300 grad. (a) Equiaxial voids in NaCl+KBF₄ (0.03 mol %) irradiated at 100 °C; latent heat of melting (LHM) of metallic Na is 5.6 J/g; (b) "penny-shaped" voids in natural rock salt samples irradiated at 70 °C; LHM of metallic Na is 2.5 J/g.

III. BIAS DRIVEN EVOLUTION OF EXTENDED DEFECTS

An edge dislocation is biased towards absorption of H centers due to stronger elastic interaction with them as compared to F centers. The dislocation bias is determined by the ratio of relaxation volumes associated with H and F centers, Ω_H/Ω_F , and is given by⁷

$$\delta_d = \ln\left(\frac{\Omega_H}{|\Omega_F|}\right) / \ln\left(\frac{2}{L_H k_H}\right), \quad (1)$$

$$L_H \equiv \frac{\mu b(1+\nu)}{3\pi kT(1-\nu)} \Omega_H,$$

where b is the host lattice spacing, μ is the shear modulus of the matrix, ν is the Poisson ratio, k_H is the square root of the total sink strength of all extended defects for H centers, and kT has its usual meaning. Therefore, dislocations are a potential source of extra F centers and V_F centers under irradiation.

Agglomeration of F centers gives rise to formation of metallic colloids, which are expected to be coherent with the host matrix as long as they are small. In this, coherent state, there exists a misfit, ϵ , which is equal to the difference between the lattice constants of the colloid and that of the host lattice. Positive (or negative) misfit means that colloid is under compressive (or tensile) stress, which influences its bias towards absorption of H centers:

$$\sigma_{rr} = \sigma_\epsilon \equiv -\frac{3K_C\epsilon}{1+3K_C/4\mu}, \quad (2)$$

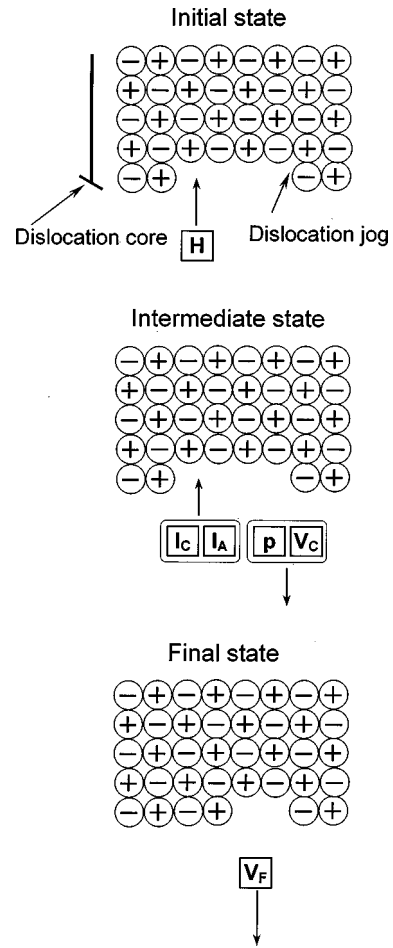


FIG. 2. Production of the V_F center as a result of absorption of an H center by an edge dislocation. When an H center approaches the dislocation, it displaces a lattice cation and forms with it a stoichiometric interstitial pair, $i_A + i_C$, where i_A and i_C are the anion and cation interstitials, respectively, and an H center is $i_A + p$ (i.e., an interstitial anion plus a hole, p). A cation vacancy, V_C , and a hole, are produced in the same reaction. The interstitial pair joins a dislocation jog leaving behind the hole trapped at the cation vacancy, that is a V_F center.

where K_C is the colloid bulk modulus, In NaCl, considered below in more detail, coherent sodium colloids have a negative misfit of about 6% and hence, a large positive misfit bias, which in the linear approximation in σ_ϵ/μ is given by⁷

$$\delta_\epsilon \equiv \alpha^d(\sigma_\epsilon/\mu), \quad (3)$$

where α^d is the constant corresponding to the elastic-diffusion anisotropy interaction between point defects and colloids,⁷ so colloid formation is possible only if the dislocation bias, δ_d , is larger than $\delta_\epsilon \approx 0.55$. The difference $\delta_d - \delta_\epsilon$ is the effective driving force for colloid growth. It is estimated to be about 0.15 for NaCl (see Table I).

Nucleation of halogen bubbles can start as the result of recombination of V_F centers, the rate of which is proportional to the square of V_F center concentration. The steady-state concentration of point defects is inversely proportional to their mobility. The mobility of V_F centers is close to that of F centers (their migration activation energies are 0.7 and 0.8 eV, respectively), which is much lower than the mobility of H centers having a migration energy of 0.1 eV. Accord-

TABLE I. Material parameters of NaCl and Na colloids used in calculations.

Parameter	Value
Diffusion coefficient of H centers, $\text{m}^2 \text{s}^{-1}$	$10^{-6} \exp(-0.1 \text{ eV/kT})$
Diffusion coefficient of F centers, $\text{m}^2 \text{s}^{-1}$	$10^{-6} \exp(-0.8 \text{ eV/kT})$
Diffusion coefficient of V_F centers, $\text{m}^2 \text{s}^{-1}$	$10^{-6} \exp(-0.69 \text{ eV/kT})$
Matrix shear modulus, μ , Gpa	15
Colloid bulk modulus, K_C , Gpa	20
Ratio of relaxation volumes of H and F centers, Ω_H/Ω_F	5
Dislocation bias, δ_d	0.7
Colloid misfit, ϵ	0.06
Misfit bias, δ_ϵ	0.55
Elastic-diffusion anisotropy interaction constant, α^d	4

ingly, the recombination of V_F centers is much stronger than that of H centers and is more likely to provide immobile molecular centers. When several H centers come to such a center they combine to form a halogen bubble which “digs its own hole” in the lattice by punching out a perfect self-interstitial loop (SIA loop). This process is exactly analogous to the loop punching from helium bubbles in metals.^{8,9} The threshold pressure for the loop punching is inversely proportional to the bubble radius^{8,10} and can be very high for small bubbles. High pressure induces a large positive addition to the bubble bias⁷ so that a small halogen bubble has a higher bias for H centers than the mean bias of the system. It means that bubbles initially can absorb surplus H centers and grow via SIA-loop punching, which is an *additional driving force* for the separation of the H and F centers into bubbles and metal colloids.

At later stages of radiolysis, the bubble bias decreases, and surplus F centers start to arrive at the bubble surface and recombine with V_F centers producing stoichiometric vacancy pairs that would increase the bubble size and so decrease the pressure below the threshold level for loop punching. After that, the bubble pressure is determined both by the number of halogen molecules and the number of vacancy pairs in it via the equation of state. Accordingly, the bubble evolution takes place in the two-dimensional phase space of the number of halogen molecules, n_{gas} , and the number of vacancy pairs, n_{vac} , as it is schematically shown in Fig. 3 (see also Ref. 11 for the underlying equations). Below some critical numbers of halogen molecules, $n_{\text{gas}}^* \approx 200-300$,¹¹ a bubble is forced to occupy a stable position along the curve in the “valley” where its bias is equal to the mean bias of the system, and both components of the bubble growth rate are zero. A gradual decrease of the mean bias, which is due to the colloid growth, makes the bubbles move adiabatically along the curve until they reach a critical point, beyond which n_{vac} would increase inexorably at n_{gas} remaining constant. Thus a conversion of bubbles to voids would take place after some threshold irradiation dose of about 40 grad, as is shown in Fig. 4. It can be seen that there is no saturation of colloid growth, although voids can grow much faster than colloids since they have no misfit bias.

Figure 5(a) shows the calculated and measured dose dependencies of the sodium latent heat of melting (LHM) at 100 °C. The LHM is proportional to the colloid volume fraction, which can be seen to correlate with void parameters in

Figs. 5(b)–5(d) measured at temperatures ranging from 60 to 130 °C. The experimental data appear to be in agreement with the calculations done assuming the experimentally observed void formation rate. In this case, there is no saturation of colloid growth, and besides, for doses higher than 100 Grad, the void dimensions may exceed the mean distance, first, between bubbles and then between colloids (R_{expl} in Fig. 4) resulting in their collisions with voids. Collisions with bubbles fill the voids with gas, and subsequent collisions with colloids bring the halogen gas and metal to a back reaction inside the voids. Such a sudden release of stored energy can be shown to result in a drastic rise of temperature (above 10^4 K) and gas pressure (up to 1 GPa) within voids,¹² which may cause cracks in the matrix resulting in the material destruction, which has been observed in some of our samples.^{3,4}

In Fig. 1(b), penny shaped voids are shown, which are

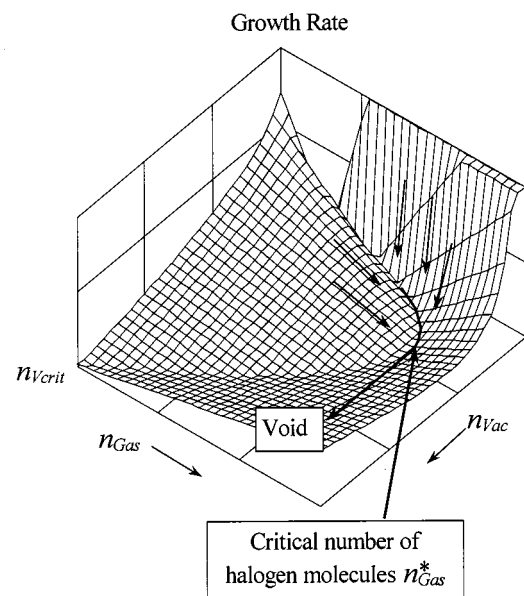


FIG. 3. The evolution path of bubbles resulting in their conversion to voids (Ref. 11). Below the critical number of halogen molecules, n_{gas}^* , the bubbles move slowly along the valley, which provide the only stable path towards the point where the critical number of halogen molecules is reached. After the point is reached, the number of vacancies starts to increase, while the number of gas molecules stays constant. n_{Vcrit} is the critical number of vacancies required for growth of an empty void ($n_{\text{gas}}=0$).

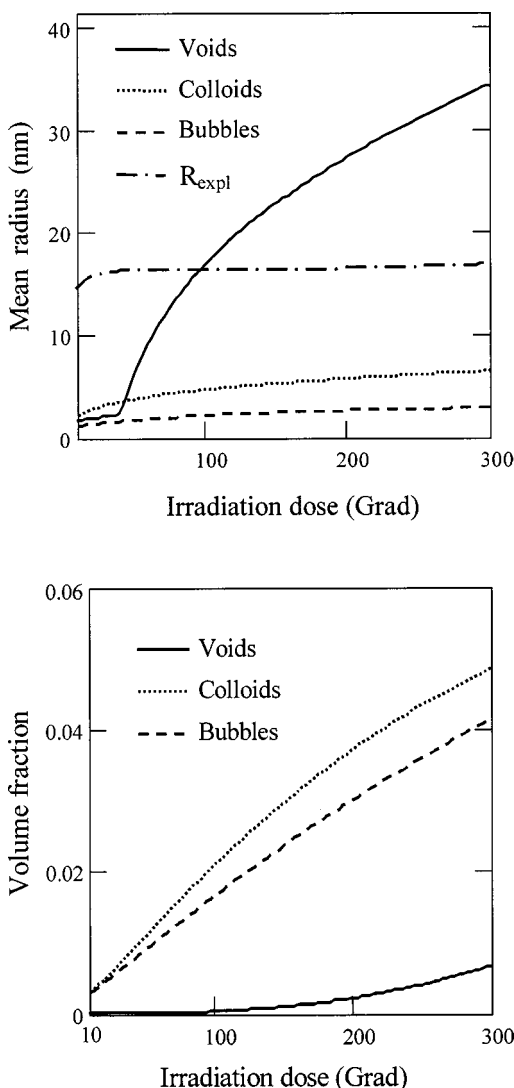


FIG. 4. Calculated dose dependence of the volume fractions (right-hand side) and mean radii (left-hand side) of extended defects in NaCl, according to Ref. 11. R_{expl} is the mean distance between colloids. At $R_V > R_{\text{expl}}$, colloids start to be captured by growing voids, which would bring the halogen gas and metal to a back reaction inside the voids.

probably formed as a result of cleavage along (100) planes due to an explosive increase of the pressure.

IV. SUMMARY

The presented scenario of the evolution of radiation-induced stored energy in rock salt is in a marked contrast with that predicted by previous models reviewed by Soppe *et al.*¹³ The main conclusion there was a *saturation* of the stored energy with increasing irradiation dose due to a back reaction between F centers and dispersed molecular centers as was originally proposed by Lidiard.¹⁴ However, systematic experiments on many (pure, doped, and natural rock salt) heavily irradiated samples have shown that with increasing dose the stored energy value increases without any sign of saturation.¹⁵ Besides, the model of dispersed molecular centers is in contradiction with early observations of halogen

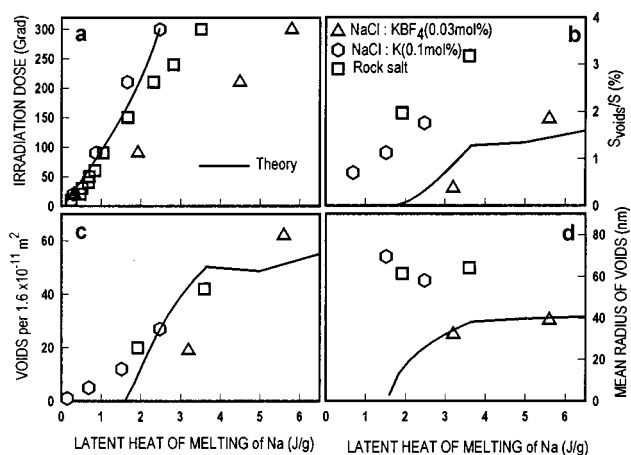


FIG. 5. Comparison between experiment (Refs. 3 and 4) and calculations (Ref. 11) based on the present theory. (a) Measured and calculated dependence of LHM of metallic Na, which is proportional to the colloid fraction, on irradiation dose at $K=240$ Mrad/h and $T=100$ °C. (b)–(d) Void mean parameters [volume fraction (b), number density (c) and mean radius (d)] against LHM measured after irradiation up to 300 grad (symbols) for different dopants and temperatures (from 60 to 130 °C) and calculated (curves) assuming dislocation density $\rho_d=10^{14}$ m⁻², and void formation rate $dN_V/dKt=2 \times 10^{17}$ Grad⁻¹ m⁻³.

bubbles after a high dose irradiation,¹⁶ as well as with recent observations of large voids.^{3,4} We would like to conclude that the amount of radiation damage in alkali halides should be evaluated with an account of vacancy void formation, which strongly affects the radiation stability of material.

ACKNOWLEDGMENTS

This study is supported by the Dutch Ministry of Economic Affairs and by the NATO Linkage Grant No. CRG.LG 973314.

- ¹A. B. Lidiard, Comments Solid State Phys. **8**, 73 (1978).
- ²L. W. Hobbs, A. E. Hughes, and Pooley, Proc. R. Soc. London, Ser. A **332**, 167 (1973).
- ³D. I. Vainshtein, C. Altena, and H. W. Den Hartog, Mater. Sci. Forum **239-241**, 607 (1997).
- ⁴H. W. Den Hartog and D. I. Vainshtein, Mater. Sci. Forum **239-241**, 611 (1997).
- ⁵D. I. Vainshtein, V. I. Dubinko, A. A. Turkin, and H. W. den Hartog, presented at EURODIM'98, Keele, 1998.
- ⁶U. Jain and A. B. Lidiard, Philos. Mag. **35**, 245 (1977).
- ⁷V. I. Dubinko, J. Nucl. Mater. **206**, 1 (1993).
- ⁸G. W. Greenwood, A. J. E. Foreman, and D. E. Rimmer, J. Nucl. Mater. **4**, 305 (1983).
- ⁹J. H. Evans, A. Van Veen, and L. M. Caspers, Radiat. Eff. **78**, 611 (1983).
- ¹⁰V. I. Dubinko, V. V. Slezov, A. V. Tur, and V. V. Yanovskij, Radiat. Eff. **100**, 85 (1986).
- ¹¹V. I. Dubinko, A. A. Turkin, D. I. Vainshtein, and H. W. den Hartog, J. Nucl. Mater. (to be published).
- ¹²D. I. Vainshtein, V. I. Dubinko, A. A. Turkin, and H. W. den Hartog, submitted to the Tenth International Conference on Radiation Effects in Insulators (REI-10), 18–23 July 1999, Jena, Germany.
- ¹³W. J. Soppe, H. Donker, A. Garcia Celma, and J. Prij, J. Nucl. Mater. **217**, 1 (1994).
- ¹⁴A. B. Lidiard, Philos. Mag. **39**, 647 (1979).
- ¹⁵H. W. Den Hartog, J. C. Groote, and J. R. W. Weerkamp, Radiat. Eff. Defects Solids **139**, 1 (1996).
- ¹⁶L. W. Hobbs and A. E. Hughes, Radiation Damage in Diatomic Materials at High Doses, Harwell Report No. AERE-R8092 (1975).